


adhesive

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any substance that is capable of holding materials together in a functional manner by surface attachment that resists separation. "Adhesive" as a general term includes cement, mucilage, glue, and paste—terms that are often used interchangeably for any organic material that forms an adhesive bond. Inorganic substances such as portland cement also can be considered adhesives, in the sense that they hold objects such as bricks and beams together through surface attachment, but this article is limited to a discussion of organic adhesives, both natural and synthetic.

Natural adhesives have been known since antiquity. Egyptian carvings dating back 3,300 years depict the gluing of a thin piece of veneer to what appears to be a plank of sycamore. Papyrus, an early nonwoven fabric, contained fibres of reedlike plants bonded together with flour paste. Bitumen, tree pitches, and beeswax were used as sealants (protective coatings) and adhesives in ancient and medieval times. The gold leaf of illuminated manuscripts was bonded to paper by egg white, and wooden objects were bonded with glues from fish, horn, and cheese. The technology of animal and fish glues advanced during the 18th century, and in the 19th century rubber- and nitrocellulose-based cements were introduced. Decisive advances in adhesives technology, however, awaited the 20th century, during which time natural adhesives were improved and many synthetics came out of the laboratory to replace natural adhesives in the marketplace. The rapid growth of the aircraft and aerospace industries during the second half of the 20th century had a profound impact on adhesives technology. The demand for adhesives that had a high degree of structural strength and were resistant to both fatigue and severe environmental conditions led to the development of high-performance materials, which eventually found their way into many industrial and domestic applications.

This article begins with a brief explanation of the principles of adhesion and then proceeds to a review of the major classes of natural and synthetic adhesives.

Adhesion

In the performance of adhesive joints, the physical and chemical properties of the adhesive are the most important factors. Also important in determining whether the adhesive joint will perform adequately are the types of adherend (that is, the components being joined—e.g., metal alloy, plastic, composite material) and the nature of the surface pretreatment or primer. These three factors—adhesive, adherend, and surface—have an impact on the service life of the bonded structure. The mechanical behaviour of the bonded structure in turn is influenced by the details of the joint design and by the way in which the applied loads are transferred from one adherend to the other.

Implicit in the formation of an acceptable adhesive bond is the ability of the adhesive to wet and spread on the adherends being joined. Attainment of such interfacial molecular contact is a necessary first step in the formation of strong and stable adhesive joints. Once wetting is achieved, intrinsic adhesive forces are generated across the interface through a number of mechanisms. The precise nature of these mechanisms have been the object of physical and chemical study since at least the 1960s, with the result that a number of theories of adhesion exist. The main mechanism of adhesion is explained by the adsorption theory, which states that substances stick primarily because of intimate intermolecular contact. In adhesive joints this contact is attained by intermolecular or valence forces exerted

by molecules in the surface layers of the adhesive and adherend.

In addition to adsorption, four other mechanisms of adhesion have been proposed. The first, mechanical interlocking, occurs when adhesive flows into pores in the adherend surface or around projections on the surface. The second, interdiffusion, results when liquid adhesive dissolves and diffuses into adherend materials. In the third mechanism, adsorption and surface reaction, bonding occurs when adhesive molecules adsorb onto a solid surface and chemically react with it. Because of the chemical reaction, this process differs in some degree from simple adsorption, described above, although some researchers consider chemical reaction to be part of a total adsorption process and not a separate adhesion mechanism. Finally, the electronic, or electrostatic, attraction theory suggests that electrostatic forces develop at an interface between materials with differing electronic band structures. In general, more than one of these mechanisms play a role in achieving the desired level of adhesion for various types of adhesive and adherend.

In the formation of an adhesive bond, a transitional zone arises in the interface between adherend and adhesive. In this zone, called the interphase, the chemical and physical properties of the adhesive may be considerably different from those in the noncontact portions. It is generally believed that the interphase composition controls the durability and strength of an adhesive joint and is primarily responsible for the transference of stress from one adherend to another. The interphase region is frequently the site of environmental attack, leading to joint failure.

The strength of adhesive bonds is usually determined by destructive tests, which measure the stresses set up at the point or line of fracture of the test piece. Various test methods are employed, including peel, tensile lap shear, cleavage, and fatigue tests. These tests are carried out over a wide range of temperatures and under various environmental conditions. An alternate method of characterizing an adhesive joint is by determining the energy expended in cleaving apart a unit area of the interphase. The conclusions derived from such energy calculations are, in principle, completely equivalent to those derived from stress analysis.

Adhesive materials

Virtually all synthetic adhesives and certain natural adhesives are composed of **polymers**, which are giant molecules, or macromolecules, formed by the linking of thousands of simpler molecules known as monomers. The formation of the polymer (a chemical reaction known as polymerization) can occur during a "cure" step, in which polymerization takes place simultaneously with adhesive-bond formation (as is the case with epoxy resins and cyanoacrylates), or the polymer may be formed before the material is applied as an adhesive, as with **thermoplastic** elastomers such as styrene-isoprene-styrene block copolymers. Polymers impart strength, flexibility, and the ability to spread and interact on an adherend surface—properties that are required for the formation of acceptable adhesion levels.

Natural adhesives

Natural adhesives are primarily of animal or vegetable origin. Though the demand for natural products has declined since the mid-20th century, certain of them continue to be used with wood and paper products, particularly in corrugated board, envelopes, bottle labels, book bindings, cartons, furniture, and laminated film and foils. In addition, owing to various environmental regulations, natural adhesives derived from renewable resources are receiving renewed attention. The most important natural products are described below.

Animal glue

The term animal glue usually is confined to glues prepared from mammalian collagen, the principal protein constituent of skin, bone, and muscle. When treated with acids, alkalies, or hot water, the normally insoluble collagen slowly becomes soluble. If the original protein is pure and the conversion process is mild, the high-molecular-weight product is called gelatin and may be used for food or photographic products. The lower-molecular-weight material produced by more vigorous processing is normally less pure and darker in colour and is called animal glue.

Animal glue traditionally has been used in wood joining, book bindery, sandpaper manufacture, heavy gummed tapes, and similar applications. In spite of its advantage of high initial tack (stickiness), much animal glue has been modified or entirely replaced by synthetic adhesives.

Casein glue

This product is made by dissolving casein, a protein obtained from milk, in an aqueous alkaline solvent. The degree and type of alkali influences product behaviour. In wood bonding, casein glues generally are superior to true animal glues in moisture resistance and aging characteristics. Casein also is used to improve the adhering characteristics of paints and coatings.

Blood albumen glue

Glue of this type is made from serum albumen, a blood component obtainable from either fresh animal blood or dried soluble blood powder to which water has been added. Addition of alkali to albumen-water mixtures improves adhesive properties. A considerable quantity of glue products from blood is used in the plywood industry.

Starch and dextrin

Starch and dextrin are extracted from corn, wheat, potatoes, or rice. They constitute the principal types of vegetable adhesives, which are soluble or dispersible in water and are obtained from plant sources throughout the world. Starch and dextrin glues are used in corrugated board and packaging and as a wallpaper adhesive.

Natural gums

Substances known as natural gums, which are extracted from their natural sources, also are used as adhesives. Agar, a marine-plant colloid (suspension of extremely minute particles), is extracted by hot water and subsequently frozen for purification. Algin is obtained by digesting seaweed in alkali and precipitating either the calcium salt or alginic acid. Gum arabic is harvested from acacia trees that are artificially wounded to cause the gum to exude. Another exudate is natural rubber latex, which is harvested from *Hevea* trees. Most gums are used chiefly in water-remoistenable products.

Synthetic adhesives

Although natural adhesives are less expensive to produce, most important adhesives are synthetic. Adhesives based on synthetic resins and rubbers excel in versatility and performance. Synthetics can be produced in a constant supply and at constantly uniform properties. In addition, they can be modified in many ways and are often

combined to obtain the best characteristics for a particular application.

The polymers used in synthetic adhesives fall into two general categories—thermoplastics and thermosets. **Thermoplastics** provide strong, durable adhesion at normal temperatures, and they can be softened for application by heating without undergoing degradation. Thermoplastic resins employed in adhesives include nitrocellulose, polyvinyl acetate, vinyl acetate-ethylene copolymer, polyethylene, polypropylene, polyamides, polyesters, acrylics, and cyanoacrylics.

Thermosetting systems, unlike thermoplastics, form permanent, heat-resistant, insoluble bonds that cannot be modified without degradation. Adhesives based on thermosetting polymers are widely used in the aerospace industry. Thermosets include phenol formaldehyde, urea formaldehyde, unsaturated polyesters, epoxies, and polyurethanes. **Elastomer-based** adhesives can function as either thermoplastic or thermosetting types, depending on whether cross-linking is necessary for the adhesive to perform its function. The characteristics of elastomeric adhesives include quick assembly, flexibility, variety of type, economy, high peel strength, ease of modification, and versatility. The major elastomers employed as adhesives are natural rubber, butyl rubber, butadiene rubber, styrene-butadiene rubber, nitrile rubber, silicone, and neoprene.

An important challenge facing adhesive manufacturers and users is the replacement of adhesive systems based on organic solvents with systems based on **water**. This trend has been driven by restrictions on the use of volatile organic compounds (VOC), which include solvents that are released into the atmosphere and contribute to the depletion of ozone. In response to environmental regulation, adhesives based on aqueous emulsions and dispersions are being developed, and solvent-based adhesives are being phased out.

The polymer types noted above are employed in a number of functional types of adhesives. These functional types are described below.

Contact cements

Contact adhesives or cements are usually based on solvent solutions of neoprene. They are so named because they are usually applied to both surfaces to be bonded. Following evaporation of the solvent, the two surfaces may be joined to form a strong bond with high resistance to shearing forces. Contact cements are used extensively in the assembly of automotive parts, furniture, leather goods, and decorative laminates. They are effective in the bonding of plastics.

Structural adhesives

Structural adhesives are adhesives that generally exhibit good load-carrying capability, long-term durability, and resistance to heat, solvents, and fatigue. Ninety-five percent of all structural adhesives employed in original equipment manufacture fall into six structural-adhesive families: (1) epoxies, which exhibit high strength and good temperature and solvent resistance, (2) **polyurethanes**, which are flexible, have good peeling characteristics, and are resistant to shock and fatigue, (3) **acrylics**, a versatile adhesive family that bonds to oily parts, cures quickly, and has good overall properties, (4) anaerobics, or surface-activated acrylics, which are good for bonding threaded metal parts and cylindrical shapes, (5) **cyanoacrylates**, which bond quickly to plastic and rubber but have limited temperature and moisture resistance, and (6) **silicones**, which are flexible, weather well out-of-doors, and provide good sealing properties. Each of these families can

be modified to provide adhesives that have a range of physical and mechanical properties, cure systems, and application techniques.

Polyesters, polyvinyls, and phenolic resins are also used in industrial applications but have processing or performance limitations. High-temperature adhesives, such as polyimides, have a limited market.

Hot-melt adhesives

Hot-melt adhesives are employed in many nonstructural applications. Based on thermoplastic resins, which melt at elevated temperatures without degrading, these adhesives are applied as hot liquids to the adherend. Commonly used polymers include polyamides, polyesters, ethylene-vinyl acetate, polyurethanes, and a variety of block copolymers and elastomers such as butyl rubber, ethylene-propylene copolymer, and styrene-butadiene rubber.

Hot-melts find wide application in the automotive and home-appliance fields. Their utility, however, is limited by their lack of high-temperature strength, the upper use temperature for most hot-melts being in the range of 40°-65° C (approximately 100°-150° F). In order to improve performance at higher temperatures, so-called structural hot-melts—thermoplastics modified with reactive urethanes, moisture-curable urethanes, or silane-modified polyethylene—have been developed. Such modifications can lead to enhanced peel adhesion, higher heat capability (in the range of 70°-95° C [160°-200° F]), and improved resistance to ultraviolet radiation.

Pressure-sensitive adhesives

Pressure-sensitive adhesives, or PSAs, represent a large industrial and commercial market in the form of adhesive tapes and films directed toward packaging, mounting and fastening, masking, and electrical and surgical applications. PSAs are capable of holding adherends together when the surfaces are mated under briefly applied pressure at room temperature. (The difference between these adhesives and contact cements is that the latter require no pressure to bond.)

Materials used to formulate PSA systems include natural and synthetic rubbers, thermoplastic elastomers, polyacrylates, polyvinylalkyl ethers, and silicones. These polymers, in both solvent-based and hot-melt formulations, are applied as a coating onto a substrate of paper, cellophane, plastic film, fabric, or metal foil. As solvent-based adhesive formulations are phased out in response to environmental regulations, water-based PSAs will find greater use.

Ultraviolet-cured adhesives

Ultraviolet-cured adhesives became available in the early 1960s but developed rapidly with advances in chemical and equipment technology during the 1980s. These types of adhesive normally consist of a monomer (which also can serve as the solvent) and a low-molecular-weight prepolymer combined with a photoinitiator. Photoinitiators are compounds that break down into free radicals upon exposure to ultraviolet radiation. The radicals induce polymerization of the monomer and prepolymer, thus completing the chain extension and cross-linking required for the adhesive to form. Because of the low process temperatures and very rapid polymerization (from 2 to 60 seconds), ultraviolet-cured adhesives are making rapid advances in the electronic, automotive, and medical areas. They consist mainly of acrylated formulations of silicones, urethanes, and methacrylates. Combined ultraviolet-heat-curing formulations also exist.

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